

Review

Methods of analysis of dithiocarbamate pesticides: a review[†]

Ashok Kumar Malik* and Werner Faubel

Forschungszentrum Karlsruhe, Institut für Instrumentelle Analytik, PO Box 3640, D-76021, Karlsruhe, Germany

Abstract: This review incorporates a brief introduction to methods for the analysis of dithiocarbamate pesticides followed by a more detailed discussion of individual methods. Determination of dithiocarbamate residues from foodstuffs, water and commercial samples and in various environmental samples using different techniques is a key feature.

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1 INTRODUCTION

Dithiocarbamates are important organosulfur compounds¹ and have a variety of applications² in agriculture as pesticides, as well as in the rubber industry as vulcanisation accelerators and antioxidants. Because they have strong metal binding capacity³ they can act as inhibitors of enzymes and have a profound effect on biological systems, so are widely used in medicine and agriculture. The biological activity of the dithiocarbamates is increased when they are in the form of heavy metal salts. The most serious and persistent problem associated with their growing use as fungicides has been the amount of residues left on food and fodder. These residues are highly mobile in soil and can leach into ground-water, so may be a potential health hazard. Therefore, their residues must be closely checked since their persistent, as well as cumulative, action may be hazardous. Some of the most-used dithiocarbamate fungicides are dibam (sodium dimethyldithiocarbamate), thiram (tetramethylthiuram disulfide), ziram (zinc bis(dimethyldithiocarbamate)), nabam (disodium ethylenebis(dithiocarbamate)), mancozeb (manganese/zinc ethylenebis(dithiocarbamate)), maneb (manganese ethylenebis(dithiocarbamate)), zineb (zinc ethylenebis(dithiocarbamate)), and ferbam (iron tris(dimethyldithiocarbamate)).

During the last thirty years analysis of dithiocarbamates has been the subject of some monographs (eg Reference 4) and of a review.⁵ Their increasing use, advances in analytical techniques and development of

more sensitive methods, were considered to warrant a review of modern analytical methods.

2 ANALYTICAL METHODS

2.1 Spectrophotometric techniques

Taguchi *et al*⁶ proposed a simple and rapid preconcentration and spectrophotometric method for the determination of traces of thiuram in water using a solvent-soluble membrane filter. Water samples containing $<160 \mu\text{g litre}^{-1}$ of thiuram were acidified with sulfuric acid; addition of a large excess of copper(II) and ascorbic acid at pH 6 resulted in the development of a light-yellow complex. This complex was retained rapidly and quantitatively on a cellulose nitrate membrane filter on filtration under suction. The filter was dried quickly with a hair dryer and dissolved in 2-methoxyethanol (3 ml) containing a small volume of concentrated sulfuric acid, and the solution was heated in a hot-water bath for about 30 s. The colour of the complex became deep-yellow, showing an absorption maximum at 390 nm. The absorbance of the solution was measured at the absorption maximum against a reagent blank. Beer's relationship was obeyed over the concentration range from 50 to $160 \mu\text{g litre}^{-1}$ of thiuram. The detection limit was $1 \mu\text{g litre}^{-1}$ for three times the standard deviation of the blank basis. High concentrations of Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Al^{3+} , Cl^- , SO_4^{2-} and NO_3^- , and levels of $\text{Fe}^{3+} < 1 \text{ mg litre}^{-1}$ did not interfere with the determination. Satisfactory

* Correspondence to: Ashok Kumar Malik, Institut für Instrumentelle Analytik, Forschungszentrum Karlsruhe, PO Box 3640, D-76021, Karlsruhe, Germany

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recoveries of thiuram added to river water and ground water were reported.

A rapid, simple, direct and sensitive method was developed by Malik *et al*⁷ for the determination of thiram (tetramethylthiuram disulfide) based on the formation of a copper dimethyldithiocarbamate complex, which was rendered water-soluble by the cationic surfactant, cetyltrimethylammonium bromide (CTAB). The method was applied for the determination of thiram in synthetic mixtures, grain (wheat) samples and vegetables.

The determination of carbon disulfide from residues of dithiocarbamates and thiuram disulfide fungicides by the spectrometric method DFG S 15 was tested satisfactorily in interlaboratory studies organised by the German Working Group 'Pesticide Residues' of the Gesellschaft Deutscher Chemiker (GDCh).⁸ Mean recoveries of 99 and 86%, respectively, have been obtained when spiking apples and potatoes with maneb (3.8 mg kg⁻¹, equivalent to 2.18 mg kg⁻¹ CS₂) and chicory with thiram (0.45 mg kg⁻¹, equivalent to 0.28 mg kg⁻¹ CS₂). The relative standard deviations fluctuated between 13 and 17% and are, therefore—according to IUPAC criteria—quite acceptable for this type of analysis.

Kapoor, Sharma and Rao⁹ reported a direct spectrophotometric method for ferric dimethyldithiocarbamate (ferbam) by complexation with 4-(2-pyridylazo)resorcinol in the pH range 8.5–10.5. The sensitivity of the method was enhanced by the addition of a micellar solution of Triton X-100. Beer's law was obeyed over the concentration range 0.5–10.2 µg ml⁻¹. The values of molar absorptivity and Sandell's sensitivity were $3.0 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and $0.0139 \text{ µg cm}^{-3}$, respectively. The method was applied for the determination of ferbam in commercial samples, crops and grains in the presence of various other ions, dithiocarbamates and xanthates.

Another spectrophotometric method for the determination of ferbam, developed by Malik and Rao,¹⁰ involved converting it into an iron-1, 10-phenanthroline complex, which was then adsorbed onto microcrystalline naphthalene in the presence of tetraphenylborate, and the absorbance then measured at 515 nm. The molar absorptivity of the complex was $1.2 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. The reported method was applied for the determination of ferbam in various commercial samples, in mixtures containing various dithiocarbamates and in foodstuffs.

A spectrophotometric method was reported by Deb *et al*¹¹ for the determination of zinc dimethyldithiocarbamate (ziram) using hydroxyamidine and 4-(2-pyridylazo)naphthol and was applied to commercial samples and to residues from foodstuffs.

Kesari and Gupta¹² reported a sensitive spectrophotometric method based on the evolution of carbon disulfide and colour development by leuco crystal violet used for the determination of such dithiocarbamate fungicides as thiram, ziram and zineb. Dithiocarbamate fungicides release carbon disulfide on acid

hydrolysis. This carbon disulfide was absorbed in ethanolic sodium hydroxide to form xanthate which was subsequently treated with potassium iodate and *N*-chlorosuccinimide, during which free iodine was liberated. Crystal violet dye, which has as absorbance maximum at 595 nm, was formed through selective oxidation of leuco crystal violet by liberated iodine. The colour systems obey Beer's law in the range of 0.02–0.20, 0.02–0.24 and 0.04–0.32 mg litre⁻¹ for thiram, ziram and zineb, respectively and their molar absorptivities are 9.6×10^5 , 1.1×10^6 and 6.8×10^5 (± 100) dm³ mol⁻¹ cm⁻¹, respectively. The method was successfully applied to the determination of these dithiocarbamate fungicides in various environmental samples.

2.2 Chromatographic methods

After a comparative study of conventional reversed phase and micellar liquid chromatography Garcia *et al*¹³ devised a method for the determination of the fungicide thiram in river water which was based on the use of micelles of CTAB. The extraction/concentration of thiram with a C-18 cartridge was followed by separation on a C-18 reversed-phase column with a mobile phase of acetonitrile (200 ml litre⁻¹) + CTAB (0.01 M) in phosphate buffer (pH 6.3), and detection at 254 nm. The method allows the determination of thiram in the presence of other water-soluble dithiocarbamate fungicides (nabam, ziram and ferbam) with a limit of detection of 36 pg ml⁻¹ for a typical 20-fold preconcentration.

Capillary electrophoresis (CE) was used by Rossi and Rotilio¹⁴ for the qualitative and quantitative analysis of 11 compounds within the carbamate, thio-carbamate and dithiocarbamate classes of pesticides, the analytes being separated using micellar electrokinetic chromatography (MEKC). Analyses were performed using an uncoated fused silica column with borate buffer containing sodium dodecyl sulfate (SDS) and methanol (100 ml litre⁻¹) at basic pH, and UV detection at 230 nm; addition of methanol to the buffer improved the separation and affected intrinsic migration of analytes. The working standard solutions were prepared in acetonitrile + water (1 + 1 by volume). Although these compounds are structurally different, with diverse chemical properties, such as polarity and solubility, good separation and sensitivity were obtained. Moreover, good recovery of carbamates was obtained from tap-water using a styrene-divinylbenzene polymer column with the solid phase extraction (SPE) technique.

A simple and sensitive capillary electrophoretic method was developed by Malik *et al*¹⁵ for the separation and determination of disodium ethylenebis(dithiocarbamate) (nabam) and sodium diethyldithiocarbamate (NaDDC) in boric acid buffer. The separation is dependent on pH and nature of the buffer and the detection limits (S/N=3) were $1.56 \times 10^{-6} \text{ mol dm}^{-3}$ and $2.48 \times 10^{-6} \text{ mol dm}^{-3}$ with a linear calibration range of three orders of magnitude for

nabam and NaDDC, respectively. The method was applied successfully to the direct analysis of water and wheat samples spiked with nabam.

A method was developed by Nitowski *et al*¹⁶ for the determination of sodium dimethyldithiocarbamate using capillary electrophoresis with a UV detector. The relative standard deviations for the analysis of the compound were 2.7 and 12.8% for 528 and 37 $\mu\text{g ml}^{-1}$ concentrations, respectively. The detection limit for sodium dimethyldithiocarbamate in waste water was established at 1 $\mu\text{g ml}^{-1}$ using 2-ml samples without preconcentration of the sample.

Ethylene bisdithiocarbamate (EBDC) residues were determined by Ahmad *et al*¹⁷ as carbon disulfide by an improved headspace gas-liquid chromatographic (GLC) procedure. Among 837 samples of 30 agricultural commodities tested, 43% contained residues above the detection limit for the method, including 100% of broccoli samples and 80% of cabbage, kiwifruit, and grape samples, together with 71% of cucumber samples. Most of the residues in kiwifruit were on or near the skin. Elimination of false-positive detections by the improved method was confirmed with kiwifruit in two independent procedures. Whole fruits were washed with EDTA (50 g litre⁻¹) to remove surface residues of EBDC. Analysis of washes for carbon disulfide by the headspace procedure after treatment with acidic stannous chloride and for ethylene thiourea by liquid chromatography after prolonged treatment at 60 °C qualitatively identified the EDTA-soluble residues as EBDC. Although the improved method does not produce false-positive results, peak area responses of carbon disulfide and of the internal standard thiophene are influenced by the chemical composition of the matrix. With matrices high in sugar or lipids, the apparent carbon disulfide content may be over-estimated by four-fold, so that accurate determination of EBDC residues in these sample types requires appropriate adjustments to matrixes.

A new sequential uniform design procedure was developed by Chan *et al*.¹⁸ The uniform design-based number-theoretic method, developed statistically, was used for optimisation of electrophoretic separation. The sequential procedure was introduced in order to reach the global optimisation for complete separation. The procedure was illustrated by the complete separation of standard dithiocarbamate (DTC) compounds by capillary electrophoresis. These five DTC compounds could not be separated by normal CE techniques but, by changing one variable at a time, were completely separated by the proposed procedure.

2.3 Polarographic methods

A method for the determination of thiuram was worked out using DC and DPP polarography. Various levels of thiuram were estimated in water+ethanol solutions containing sodium chlorate and water+ethanol Brdicka solutions by Zjawiony¹⁹ for the concentration range 0.02 to 100 $\mu\text{g ml}^{-1}$ with the

relative error not exceeding $\pm 5\%$. The procedure described was used to determine thiuram residues on horticultural foil and in installations employed for fungicide degradation.

A convenient and accurate analytical procedure was developed by Sharma *et al*²⁰ for the trace determination of tetramethylthiuram disulfide in commercial fungicides and rubber accelerators for the purpose of quality control. Thiuram disulfide gives a well-defined, diffusion-controlled cathodic wave in 0.01 M pyridinium perchlorate in dimethylformamide with half-wave potential -0.36 V against a saturated calomel electrode. Determination was made by normal pulse and differential pulse polarography using linear calibration plots.

A DC polarographic technique was used for the determination of the pesticide ziram in aqueous samples by Mathew *et al*²¹ based on differential pulse anodic stripping voltammetric determination of ziram zinc in rice samples using a static mercury drop electrode. The procedure developed distinguishes inorganic zinc and ziram zinc in sodium acetate+sodium chloride media. The procedure developed was suitable for the determination of concentrations of ziram as low as 10 mg litre⁻¹. The precision was 2.1% in respect of five successive determinations of ziram at 150 mg litre⁻¹.

2.4 Indicator tubes

Marchenko *et al*²² developed a method using indicator tubes for the determination of reducing agents in solutions. The reactions of ion associates formed by thiazine dyes (methylene blue and toluidine blue) and triiodide ions with reducing agents ($\text{S}_2\text{O}_3^{2-}$, SO_3^{2-} , diethyl dithiocarbamate, ethyl xanthate and ascorbic acid) in solution were studied. Indicator tubes were proposed for determining total reducing agents and ascorbic acid. The dependence of the length of the coloured zones on tube diameter, flow rate of the solution, and concentration of Triton X-100 surfactant was examined. The tubes proposed were essentially superior to commercial test kits in reproducibility and compared well with them in sensitivity and analytical range. The tubes were recommended for the determination of total reducing agents in waste water and of ascorbic acid in fruit juices.

2.5 Flow-injection fluorimetry

Nabam and metham were determined by Perezruiz *et al*²³ using a simple and sensitive flow injection fluorimetric method based on the oxidation of these compounds by thallium(III) with the simultaneous formation of fluorescent thallium(I). Linear calibration graphs were obtained between 0.25 and 2.56 $\mu\text{g ml}^{-1}$ for nabam and between 0.26 and 2.56 $\mu\text{g ml}^{-1}$ for metham. Eighty samples per hour could be processed and the method was applied for the determination of nabam and metham in spiked samples from water, wheat, barley and oats.

Table 1. Comparison of spectrophotometric methods for the determination of dithiocarbamates

No	Reagent	Dithiocarbamate pesticide	λ_{max}	Molar absorptivity 1×10^4	Linear range ($\mu\text{g ml}^{-1}$)	Reference
1	Cuprous chloride	Thiram	420	NR ^a	4–200	27
		Ferbam	385	NR	1–100	28
		Ziram	385	NR	1–100	27
2	Cupric acetate	Zineb	370	NR	5–100	29
3	Molybdenum	Thiram	420	0.15	5–110	30
		Ferbam	420	0.63	10–200	31
		Ziram	420	0.15	27–750	32
		Nabam	670	0.13	25–700	33
		Zineb	670	0.62	2–40	34
		Maneb	670	0.69	2–40	35
		Thiram	420	1.32	5–110	36–38
4	Chromium	Ferbam	420	2.10	10–20.0	
		Ziram	420	1.28	2.7–75.0	
		NaDDC	420	0.55	1.2–16.5	
		Dibam	420	0.15	0.6–19.8	
		Thiram	430	1.06	0.52–16	39
		Ferbam	430	1.46	1.0–28	40
		Ziram	430	1.59	0.8–12	39
5	Selenium	NaDDC	430	1.57	1.2–16.5	39
		Dibam	430	0.60	1–20	39
		Ziram	430	1.923	0.65–19.5	41
		Thiram	430	1.723	0.7–20.0	42
		Ziram	395	1.298	0.7–10.0	41
6	Copper(II) (adsorption on naphthalene)	Thiram	395	1.28	0.9–12.7	42
		Ziram/Zineb	520	8.36	0.1–1.7/0.12–1.9	43
		Ferbam	520	5.3	0.35–4.8	43
7	Diphenylcarbazone + pyridine	Maneb	520	6.5	0.03–2.7	44
		Ziram	550	5.06	0.2–2.2	45
		Zineb	550	5.06	0.5–2.4	45
		Maneb	550	4.10	0.37–0.75	45
8	4-(2-pyridylazo)resorcinol (PAR + TX-100)	Ferbam	530	3.00	0.5–10.2	9
9	Copper(II) + ascorbic acid	Thiram	–	–	0.05–0.160	7
10	Leuco crystal violet	Thiram	595	96	0.002–0.20	12
		Ziram	595	11	0.002–0.24	
		Zineb	595	68	0.04–0.32	
11	1,10-Phenanthroline	Ferbam	490	1.71	0.80–20.0	46
12	1,10-Phenanthroline (adsorption on naphthalene in the presence of tetraphenylborate)	Ferbam	515	1.2	2.24–37.29	10
13	Copper(II) + CTAB	Thiram	430	1.63	0.44–13.25	7

^a NR: not reported.

2.6 Biosensor

A bioenzymic sensor for the determination of dithiocarbamate fungicides was developed by Noguer and Marty²⁴ based on aldehyde dehydrogenase inhibition. The NADH formed by the oxidation of propionaldehyde by aldehyde dehydrogenase was reoxidised by diaphorase using hexacyanoferrate(III) as electron acceptor. The hexacyanoferrate(II) produced was oxidised electrochemically at a potential of 250 mV vs saturated calomel electrode (SCE). As dithiocarbamate fungicides inhibit aldehyde dehydrogenase, a decrease of the induced current was correlated to their concentration in the working medium. Aldehyde dehydrogenase and diaphorase were used in solution or entrapped in a photo-cross-linkable poly(vinyl alcohol) bearing styrylpyridinium groups. The best results were achieved using entrapped enzymes, and

the sensitivity of the sensor was improved by lowering the amount of enzyme and by increasing the contact time between the pesticide and the enzyme. Using entrapped enzymes, the detection of 1.48 mg litre⁻¹ of maneb was reported, whereas the commonly used spectrophotometric methods allow detection of only 400 mg litre⁻¹ of dithiocarbamate.

2.7 Solid phase extraction

Solid-phase extraction (SPE) using C-18 bonded-phase silica cartridges for determination of trace amounts of carbaryl, propoxur, thiram, prothion and methiocarb in water samples was studied by Morenó and Santosdelgado²⁵ and the breakthrough volume of the cartridges was established. The high enrichment factor and large injection volume admissible in the isocratic reverse-phase HPLC system

allows pesticide determination with UV detection at 220 nm even at a concentration lower than $0.05 \mu\text{g litre}^{-1}$. Purified, tap, natural and underground water samples were spiked with carbamate pesticides in the concentration range 0.16 – $16 \mu\text{g litre}^{-1}$. Large volumes of samples (up to 2 litres) were passed through C-18 cartridges and eluted with acetonitrile. The pre-concentrated samples were analysed by HPLC using a Spherisorb ODS column with a $42 + 58$ acetonitrile + water mobile phase. From replicate samples, recovery for the pesticides ranged from 79.0 to 103.7% except for thiram which was not retained. The relative standard deviation ($n=4$ at 0.16 to $1.61 \mu\text{g litre}^{-1}$ concentration level) ranged from 1.1 to 6.8. The maximum residue limits for dithiocarbamates (expressed as carbon disulfide) which are allowed by the European Union are 2 – 7 mg kg^{-1} .

3 SAFETY STANDARDS

For the last 30 years the Joint FAO/WHO Meeting on Pesticide Residues²⁶ (JMPR) has carried out toxicological evaluations and safety assessments of dithiocarbamate pesticides, continuously adjusting previous appraisals in the light of new data and advances in the understanding of the principles and mechanisms of toxic action of these compounds. The historical narrative of the evaluative process was followed by an account of the present international safety assessment status of the dithiocarbamate pesticides so far examined by the JMPR which are: ferbam, mancozeb, maneb, metiram, nabam, propineb, thiram, zineb, ziram, and the associated substances, ethylenethiourea (ETU) and propylenethiourea (PTU).

4 CONCLUSIONS

Dithiocarbamates are generally determined by carbon disulfide evolution methods which are time-consuming and neither selective nor sensitive. The maximum residue limits for dithiocarbamates (expressed as carbon disulphide) which are considered by the European Union²³ are 2 – 7 mg kg^{-1} . Among gas chromatographic, capillary electrophoretic and high pressure liquid chromatographic methods for the determination of dithiocarbamates, gas chromatographic methods are sensitive but not selective because all dithiocarbamate pesticides evolve carbon disulfide on acid decomposition. Capillary electrophoresis methods are highly selective, but at higher concentrations adsorption of dithiocarbamates on the walls of the capillary is reported. Among the spectrophotometric methods, those based on decomposition and determination of the metal ion present in the dithiocarbamate moiety in the presence of the sequestering agents are of considerable importance. A comparison of all the spectrophotometric methods is given in Table 1. A study of the degradation products of these pesticides is still needed. Thus, with increasing use of dithiocarbamates on food and fodder there is

still a need for the development of new sensitive, selective and rapid methods for their analysis.

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